FTIR Studies of the Curing Reactions of Palm Oil Alkyd–Melamine Enamels

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ABSTRACT: Three alkyds of high hydroxyl numbers with oil lengths of 21, 30, and 41 were prepared from crude palm oil. The excess hydroxyl groups provided good compatibility with melamine resins, and also served as sites for crosslinking reactions. They were made into baking enamels by blending with 20% of a commercial melamine resin. All of them could be cured at temperatures below 200°C although thermodecomposition might occur above 290°C. The dry-hard time of these enamels cured at temperatures between 140–180°C ranged from 10 to 180 min. Fourier transform infrared spectroscopy could be used to follow the major curing reactions. The absorbance of —O—H and —N—CH$_2$—OCH$_3$ groups showed significant reduction. The changes in the absorbance of these peaks with time and temperature were investigated. The predominant reaction was identified as the formation of methylene ether linkages. However, the self-condensation reactions of the amino resin and ester linkages did not occur to any noticeable extent. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2309–2315, 2001

Key words: palm oil alkyd; alkyd–melamine enamel; FTIR studies; curing reactions

INTRODUCTION

Alkyds are major synthetic resins popularly used in the paint industry because of their versatility and good performances. Alkyd-based coatings are well known for good corrosion protection, high gloss, and the ease of application even over poorly treated surfaces.[1,2]

Traditionally, alkyds having a molecular weight ranging from 40,000 to 100,000 have been produced in aliphatic or aromatic solvents at low-solids content with slight excess in hydroxyl over the carboxylic groups to avoid gelation during the synthesis. The ratio of hydroxyl equivalent to carboxylic equivalent in the initial formulation determines the maximum extent of reaction and the final average molecular weight of the alkyd.

With the advent of the regulations against air pollution, and for safety consideration, there have been continued interests in searching for alternative raw materials and new formulations to reduce the overall volatile organic compounds in surface coatings.

Two viable approaches to reducing volatile organic compounds are the developments of water-reducible alkyds and high-solid alkyds.[3] Water-reducible alkyds are usually of low molecular weight and contain sufficient acid value for neutralization with ammonium hydroxide or amine and must be hydrophilic enough to become miscible with water. By contrast, high-solids alkyds tend to have high hydroxyl numbers, less branching, and have a typical molecular weight in the range of 12,000 to 20,000.

Recently, a series of water-reducible alkyds were prepared from palm stearin.[4,5] These alkyds

have average molecular weights of around 1100 and acid values around 50, and have shown good film-forming properties as clear baking enamels from mixing with a methylated melamine resin. The film properties of the coatings varied with composition and curing temperature.[6] Alkyds modified with melamine are mainly used in industrial baking enamels for substrates such as metal cabinets, appliances, Venetian blinds, and toys. Although melamine-containing coatings have been the subject of recent reviews and research articles,[7–9] the actual mechanisms and pathways involved are still not fully understood because of the chemical complexity of the reactions.

This report describes a series of three palm oil alkyds (POA), with oil lengths of 21, 30, and 41, respectively, synthesized with high hydroxyl numbers. Although they do not have sufficient unsaturation for satisfactory air-drying properties, the excess hydroxyl groups provide good compatibility with melamine resins, and also serve as sites for crosslinking reactions with the amino resins when made into baking enamels. The predominant reaction during cure could be identified by Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

The crude palm oil was a kind gift from Golden Hope Plantation (Malaysia) Ltd. The 95% ethanol, potassium hydroxide, and potassium hydrogen phthalate were reagent grade chemicals purchased from Merck (UK). Other chemicals, as listed below, were commercial grades and were used without further purification. Phthalic anhydride was from P. T. Petrowidada, Indonesia, glycerin (99.5% PH.EUR) from Henkel Oleochemicals (Malaysia) Pte Ltd., butyl cellusolve from Dow Chemical, n-butanol from Mobil (Malaysia) Pte Ltd., lithium hydroxide from FMC Corp., and methylated melamine formaldehyde resin (Cymel 303) was from Cytec, USA.

Preparation of POA

The charged composition of each alkyd with specified oil length was formulated by calculation to give a hydroxyl excess of 92 ± 1. The resin was prepared in two steps. Alcoholysis between crude palm oil and glycerin catalyzed by LiOH was first performed at 220°C for about 30 min to form a monoglyceride. The second step was polymerization through transesterification involving additional phthalic anhydride and glycerin at 180°C. Progress of the reaction was monitored through measuring the liberated water and checking the acid number of the reaction mixture by titrating aliquot of mixture, dissolved in 50 mL of xylene/ethanol (1:1), with standardized 0.1N ethanolic KOH. When the acid number fell below 10, the heating mantle was removed immediately. The mixture was allowed to cool to 120°C before being diluted with a 1:1 mixture of n-butanol and butyl cellusolve to a final solid content of around 50%.

Formulation of Clear Enamel

Four parts by weight of the alkyd (based on dried weight) was mixed with one part by weight of Cymel 303 resin (containing 98% solid hexamethoxymethyl melamine resin) and a suitable amount of 1:1 mixture of n-butanol and butyl cellusolve to the desired solid content.

Thermal Analysis of Enamel by Differential Scanning Calorimetry (DSC)

A sample was placed in a DSC pan and dried in a vacuum oven overnight at ambient temperature before the sample was encapsulated. The sample was then mounted in the instrument and scanned at 20°C min^{-1} from 25–200°C. The same sample was then cooled down and scanned again. Calibration of the DSC instrument was described previously.[10]

Thermogravimetric Analysis (TGA)

The alkyd enamel with solvent was subjected to TGA measurement. About 7–12 mg of the sample was heated under nitrogen atmosphere from 40–800°C at a heating rate of 20°C min^{-1}.

Determination of Dry-Hard Time

A thin layer of the enamel resin was coated on a glass panel. The solvent was removed under reduced pressure in a vacuum oven at ambient temperature. The panel was placed in an oven set to the specified temperature. The surface was checked periodically until the film was dry to a stage in which the pressure that can be exerted between thumb and finger fails to move the enamel film or leave a mark behind. This was

Table I Properties of Alkyd with Oil Lengths of 21, 30, and 41

Sample Code	POA21	POA30	POA41
Oil length (%)	21	30	40
Acid number (from calculation)	7.0	7.0	7.0
Acid number (determined by titration)	9.0	3.5	5.1
Water liberated (from calculation) (mL)	49.5	44.0	35.5
Water collected (mL)	49.5	45.0	35.5
Alkyd constant[11]	1.20	1.23	1.27
Hydroxyl number (mg KOH per g alkyd)	367	340	312
Hydroxyl excess[a] (%)	92.2	93.0	93.2
Nonvolatile material (%)	46.1	57.1	50.0

[a] (Equivalent of OH − equivalent of COOH)/(equivalent of COOH) × 100% based on the initial charged amount.

recorded as the dry-hard time.[11] It is a semiquantitative measurement of the rate of cure of the coating. A faster cure rate is reflected by a shorter dry-hard time.

Reactions During Cure by FTIR

A thin film of the enamel resin was coated directly onto the sodium chloride cell and the solvent was removed under reduced pressure in a vacuum oven at ambient temperature. The cell was then placed in an oven at the specified temperature and allowed to cure for the specified time before the infrared spectrum was recorded.

RESULTS AND DISCUSSION

Properties of the POA

Basic properties of the three POA with oil lengths of 21, 30, and 41, respectively, are shown in Table I.

Curing Behavior of Enamel by DSC

The complex curing behavior of the clear enamel can be illustrated qualitatively by DSC technique. The DSC curves of the clear enamel for alkyd POA21 during and after cure are shown in Figure 1. Reactions began around 115°C and stopped around 185°C. Exothermic peaks could be attributed to heats evolved in the various crosslinking reactions while the relative sharp endothermic peaks to the heats absorbed in sudden phase changes when small molecules such as water were liberated. When the same sample was cooled down and scanned again, there was no more noticeable peaks, showing that the curing reactions were completed.

TGA of Enamel Samples

A typical TGA measurement is shown in Figure 2. The thermogram can be divided into four distinct segments corresponding to different events. AB denotes the rapid vaporization of the volatile components in the temperature range of 40–196°C. BC showed a slower rate of weight loss at 196–305°C because of slower liberation of entrapped solvent or high boiling components. The loss of some byproducts from the condensation reactions could be expected in this region. Incidentally, the mean value of points B and C agreed fairly closely with the resin content determined by a separate experiment in which a small sample was dried overnight in an oven at 120°C. Point C indicated the onset of the next rapid weight loss which occurred in the temperature range of 305 to 454°C. DE showed that the rate of degradation had slowed down at 454–602°C. After E, the sample was reduced to essentially carbon residue.
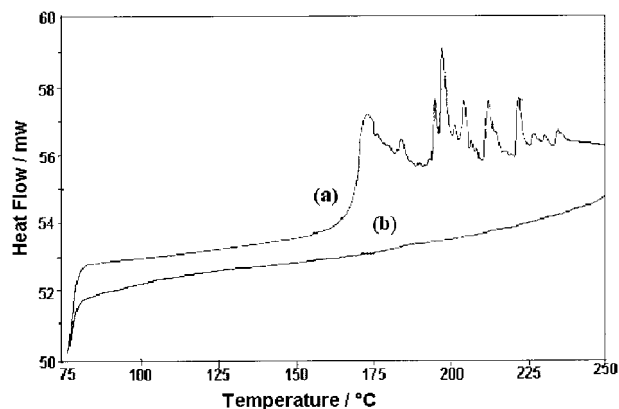

Figure 1 The DSC curves of the clear enamel for alkyd POA21, (a) during cure, and (b) after completely cured.
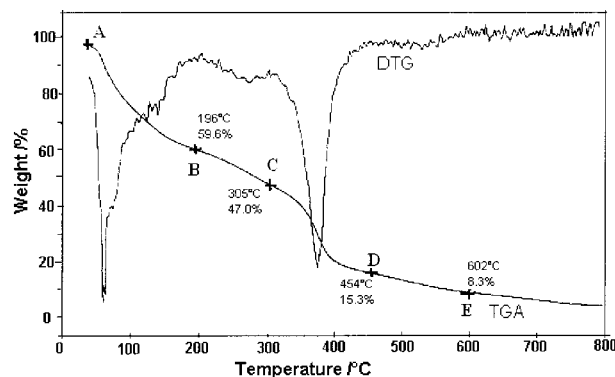
Figure 2 A typical TGA measurement on the clear enamel samples at a heating rate of 20°C min^{-1}. The thermogram can be divided into four distinct segments corresponding to different events.

Table II shows a summary of the results of TGA measurements on the three different enamels. Overall, the TGA results showed that these enamels could be cured at any temperature below 290°C without any thermal degradation.

Dry-Hard Time

From practical viewpoints, there are three important factors in the cure of resins: (i) time, (ii) temperature, and (iii) shrinkage that takes place in the resin during cure. Cure time is inversely proportional to the cure temperature. For fast production processing, it is desirable to shorten the cure time by raising the temperature, but extremely high temperature cannot be used for many applications. An optimum temperature should be chosen for reasonable cure time with minimum film defect.

In this study, cure temperatures at 140, 160, and 180°C were arbitrarily chosen to show that a wide range of dry-hard time could be achieved (Table III). As expected, the dry-hard time decreased with increasing temperature because the rate of the crosslinking reaction increases at higher temperature.

Table III Dry-Hard Time for Enamels of Alkyds with Oil Lengths of 21, 30, and 41

Alkyd	Dry-Hard Time (min)		
	140°C	160°C	180°C
POA21	40	20	10
POA30	110	40	20
POA41	180	70	40

Alkyd of higher oil length, which has lower hydroxyl number, is seen to have longer dry-hard time because the rate of reaction between hydroxyl groups of the alkyds with the methylmethoxyl groups of the melamine-formaldehyde resin is dependent on the amount of hydroxyl group. A second reason may be attributed to the lower phthalic anhydride content per gram of alkyd at higher oil length. Lower phthalic anhydride content tends to reduce the glass transition temperature of the resulting alkyd and hence would reduce the contribution to the lacquer-dry.[11]

Characteristic FTIR Peaks of Component Resins

Figure 3 shows the overlay spectra of pure melamine resin and the three POA for the purpose of identifying the characteristic peaks of these component resins in the clear enamels. In spectra of the pure alkyd, the broad band at 3440 cm^{-1} is due to O—H stretching, 2925 and 2854 cm^{-1} due to C—H stretching, 1732 cm^{-1} due to C=O stretching of COOH and overlapped with C=O of ester, 745 cm^{-1} due to C—H bending of aromatic ring contributed by phthalate units. However, in the spectrum of the Cymel 303 resin, the peak at 1557 cm^{-1} is attributed to the overlap of N—H deformation and C—N stretching, 1387 cm^{-1} due to C—H bending, and 913 cm$^-$ due to C—H rocking of —N—CH$_2$—OCH$_3$.[6] The weak band at 3350 cm^{-1} is attributed to the imino N—H stretching,

Table II TGA Data on Clear Enamels of Palm Oil Alkyds

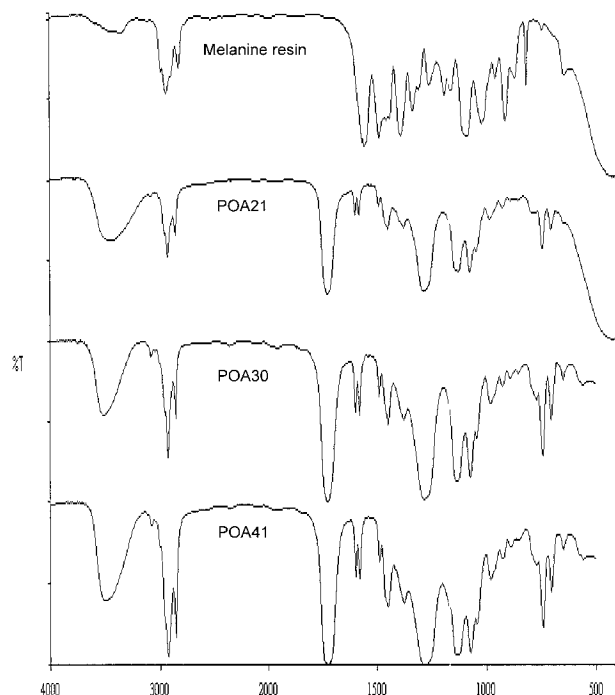| Alkyd	Resin Content (%) (at Midpoint of BC)	Dry Resin Content (%) (by Drying in Oven)	Onset of Thermal Degradation (°C)
POA21	53.4	51.4	305
POA30	60.5	60.0	297
POA41	55.1	53.4	295

Figure 3 The overlay FTIR spectra of pure melamine resin and the three POA as labeled. Samples were cast as thin liquid film on the sodium chloride cell and the solvent was removed under reduced pressure at ambient temperature.

Figure 4 The overlay FTIR spectra of enamel of POA21 cured at 180°C for 0, 20, and 60 min. Peaks that have undergone significant reduction in absorbance are marked in the figure. The absorbance peak at 745 cm^{-1} was chosen as internal reference to monitor the change in absorbance of the other peaks.

arising from a small amount of nonfully methylated melamine units.

Predominant Reaction During Cure in the Enamel

Both the alkyd and melamine resins are complex mixtures, in which each component can undergo a variety of reactions. Some of the crosslinking reactions are reversible, so that bonds might break and reform many times during cure of a coating, causing network structure to change continuously throughout the process.[7]

The enamels were cured at 140, 160, and 180°C for different time periods and their FTIR spectra recorded to monitor the changes in functional groups with cure time. Figure 4 shows the overlay spectra of enamel of POA21 cured at 180°C for 0, 20, and 60 min. Peaks at 3440, 1557, 1387, and 913 cm^{-1} showed significant reduction during cure whereas other peaks did not show any noticeable change. The aromatic peak at 745 cm^{-1} was picked as reference because the benzene ring was not expected to undergo any change during the cure. The ratio of the absorbance of a selected peak to the reference peak was taken to reflect the concentration of the functional group.
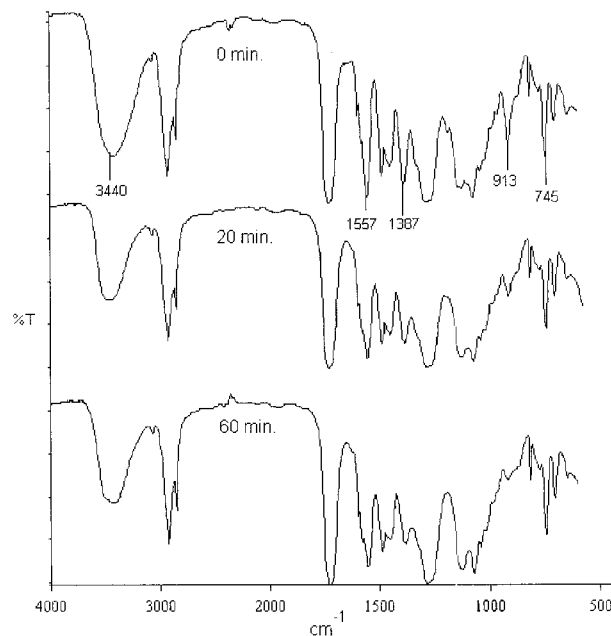
The changes in absorbance at 3440, 1557, 1387, and 913 cm^{-1} during cure of the enamels at different reaction time are shown in Tables IV–VII, respectively. With reference to Table IV, the

Table IV   Ratios of A_{3440}/A_{745} at Different Reaction Times at the Specified Temperatures

	Reaction Temperature		
Time (min)	140°C	160°C	180°C
Enamel of POA21			
0	1.45	1.43	1.43
30	1.15	0.99	0.87
60	1.05	0.90	0.87
Enamel of POA30			
0	1.27	1.24	1.27
20	1.02	1.00	0.95
40	0.98	0.92	0.89
60	0.90	0.87	0.82
Enamel of POA41			
0	1.63	1.68	1.70
30	1.33	1.26	1.20
60	1.30	1.23	1.17
90	1.21	1.17	1.08

Table V   Ratios of A_{1557}/A_{745} at Different Reaction Times at the Specified Temperatures

Time (min)	Reaction Temperature		
	140°C	160°C	180°C
Enamel of POA21			
0	2.64	2.60	2.70
30	2.44	2.36	2.26
60	2.39	2.31	2.18
Enamel of POA30			
0	4.10	3.97	3.64
20	4.02	3.88	3.44
60	3.96	3.49	3.28
Enamel of POA41			
0	3.28	3.34	3.31
30	3.15	2.92	2.82
60	2.98	2.82	2.80

Table VII   Ratios of A_{913}/A_{745} at Different Reaction Times at the Specified Temperatures

Time (min)	Reaction Temperature		
	140°C	160°C	180°C
Enamel of POA21			
0	1.08	1.02	1.03
30	0.99	0.74	0.57
60	0.83	0.61	0.42
Enamel of POA30			
0	1.21	1.26	1.29
20	1.15	1.20	1.08
40	1.09	1.17	1.00
60	1.05	1.07	0.88
Enamel of POA41			
0	1.39	1.39	1.39
30	1.29	1.27	1.16
60	1.24	1.16	1.06
90	1.14	0.99	0.91

broad band at 3440 cm^{-1} was due entirely to the intermolecular hydrogen bonded —OH group of the alkyd molecules. Contribution from imino N—H group of melamine resin was not significant as the Cymel 303 resin was nominally 100% methylated.

Results in Tables V and VI show that involvement of the melamine molecules as the peaks assigned to C—N stretching at 1557 cm^{-1}, and the C—H bending of —N—CH$_2$OCH$_3$ group at 1387 cm^{-1} had decreased slightly after cure. More significantly, changes in the peak at 913 cm^{-1}

Table VI   Ratios of A_{1387}/A_{745} at Different Reaction Times at the Specified Temperatures

Time (min)	Reaction Temperature		
	140°C	160°C	180°C
Enamel of POA21			
0	2.05	2.00	2.10
30	1.85	1.72	1.65
60	1.79	1.64	1.51
Enamel of POA30			
0	2.62	2.63	2.57
20	2.52	2.54	2.33
40	2.47	2.41	2.27
60	2.44	2.34	2.17
Enamel of POA41			
0	2.53	2.57	2.55
30	2.43	2.24	2.22
60	2.40	2.23	2.19
90	2.39	2.22	2.15

caused by C—H rocking of —N—CH$_2$OCH$_3$ were observed (Table VII). As expected, the overall rate of cure increased with the temperature.

Peaks at 1286, 1124, and 1075 cm^{-1}, which could be traced to the alkyd, remained unchanged. These peaks could not be described in terms of simple motion of specific functional groups, but as the mechanical coupling between adjacent C—O, C—C stretch, and O—H and —CH$_2$— bending mode.[12]

Various likely reactions between the alkyd and melamine resins have been discussed earlier and could be represented by Scheme 1.
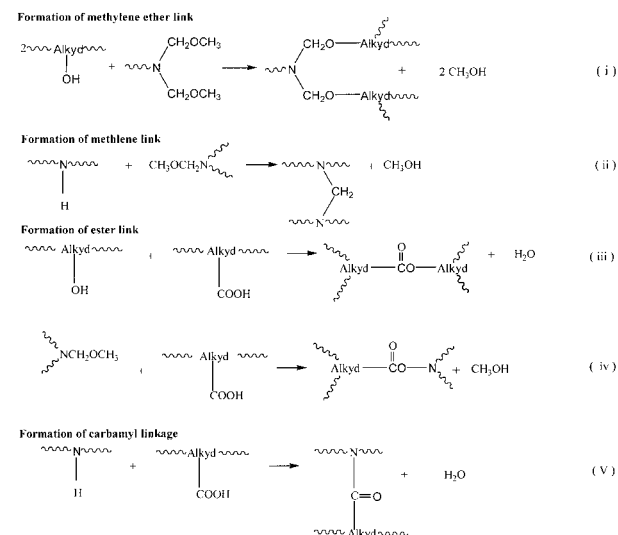
With reference to the evidence provided by FTIR, reactions (iii), (iv), and (v) were not impor-

tant because these alkyds have very low acid value. Reaction (i) was responsible for the drop in absorbance for O—H in alkyd and C—H rocking for methoxylmethyl structure in the melamine. Reaction (ii), which represents the self-condensation reaction of melamine resin, is not expected to be significant because there is very little imino N—H in the Cymel 303 resin.

CONCLUSION

The complex reactions of alkyd melamine enamels can be illustrated qualitatively by using DSC. The clear coat can be cured in the temperature range of 115–185°C. TGA results showed that the enamels did not decompose at temperatures below 290°C. FTIR could be used to follow the major crosslinking reaction during the cure. The absorbance peaks of O—H and —N—CH_2OCH_3 groups showed significant reduction during the cure. The predominant reaction has been identified as the formation of methylene ether linkages.

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